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CLEAR FABRIC SOFTENER FORMULATIONS

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[Abstract]

The object of the invention consists of fabric softener formulations based on one or more cationic surfactants and at least one other component that gives the overall formulation a water-pale and clear appearance.

Description

[0001]

The object of the invention consists of fabric softener formulations based on one or more cationic surfactants and at least one other component that gives the overall formulation a water-pale and clear appearance.

[0002]

The detergent industry has over time developed fabric softener formulations with improved rewetting capacity, high stability and a good soft feel. By far most of these formulations are sold as aqueous dispersions. Examples for the formulation of dispersions are described, among other places, in DE 37 20 331, DE 42 03 489 and EP 0 413 249.

[0003]

However, the formulations produced by the procedures described there can be produced only at high energy cost and they tend to have significant variations of viscosity, especially at high storage temperatures. In addition, it is well known that agglomerates in softener dispersions lead to the formation of spots on the treated textiles.

Amidst increased aesthetic awareness a prejudice has developed against particulate fabric softener formulations. Increasing demand for naturally clear appearing formulations has been found among consumers.

[0004]

Flowable, highly concentrated or clear softener formulations have already been described, for example in DE 33 14 677 and DE 36 08 093.

[0005]

The high concentrates described there, which as a rule contain >35% quaternary fabric softener components, however have the disadvantage that it is difficult to dilute these formulations with water or that poorly water-soluble gels arise as the highly concentrated formulation is washed into the dispensing chamber of the washing machine and uniform treatment of textiles is not guaranteed. In addition, with these highly concentrated softeners overdosages frequently occur, which leads to the formation of spots on the treated fabrics.

[0006]

For this reason the task of this invention was to avoid these disadvantages of the prior art and to make available softener formulations that, when compared to the comparable products of

the prior art, have at least as good a spectrum of action and, moreover, have a clear and water-pale appearance, that can be produced with reduced energy cost and the handling of which ensures problem-free use for the end user.

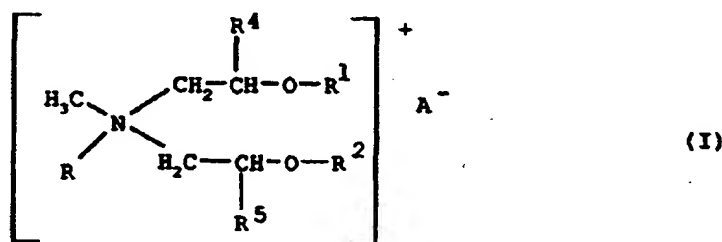
[0007]

It was now found that softener formulations consisting chiefly of cationic surfactants and 5-30 wt%, with respect to the total formulation, of another compound satisfies these requirements.

[0008]

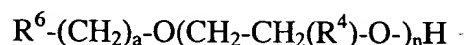
The object of the invention therefore consists of clear and water-pale fabric softener formulations containing

A) 15-35 wt% of at least one quaternary ammonium compound of the general formula (I)



and

B) 5-30 wt% of at least one compound of the general formula (II)



with the meanings

$\text{R} = -\text{CH}_3, =\text{CH}_2-\text{CH}(\text{R}^4)-\text{OR}^1, -\text{CH}_2-\text{CH}(\text{R}^5)-\text{OR}^2$ , in which  $\text{R}^4, \text{R}^5$  can be the same or different and mean H,  $-\text{CH}_3$ ,

$\text{R}^1, \text{R}^2 = \text{H}, -\text{C}(\text{O})-\text{R}^3$ , in which  $\text{R}^3$  is an optionally substituted hydrocarbon residue with 13-19 C atoms that has at least one double bond, with the stipulation that if  $\text{R} \neq \text{CH}_3$ ,  $\text{R}^1, \text{R}^2$  are a minimum of 1-1.4 times H, and if  $\text{R} = \text{CH}_3$ ,  $\text{R}^1, \text{R}^2$  are a maximum of 0.4 times H,

$\text{R}^6$  is a phenyl residue optionally containing  $\text{C}_1$ - $\text{C}_4$  alkyl groups or a branched alkyl residue with 3-6 C atoms,

$n = 0-8$ ,

$a = 0 \text{ or } 1$

A<sup>-</sup> = an anion of a quaternization agent, especially dimethyl sulfate, diethyl sulfate, methyl chloride, and

C) 0.5-18 wt% conventional auxiliary substances and additives and

D) water to 100 wt%.

[0009]

Another object of the invention consists of aqueous softeners in which methyldiethanolamine, methylethanolisopropanolamine, methyldiisopropanolamine, triisopropanolamine or triethanolamine are used as alkanolamines.

[0010]

Another object are aqueous softeners based on esters of fatty acids and alkanolamines that are converted in a mol ratio from 1:1.6 to 1:2.

[0011]

Other objects of the invention are defined by the claims.

[0012]

The quaternary compounds of general formula (I) that are used in accordance with the invention are produced by methods generally known from this field by esterification of alkanolamines like triethanolamine (TEA), methyldiethanolamine (MDEA), methyldiisopropanolamine (MDIA), methylethanolisopropanolamine (MEIPA), triisopropanolamine (TIPA) with a fatty acid followed by quaternization.

[0013]

Particularly common are ester compounds based on triethanolamine like N-methyl-N,N-bis(beta-C<sub>14-18</sub>-acyloxyethyl)-N-beta-hydroxyethylammonium methosulfate), which are sold under trade names like Tetranyl® AT 75 (trade name of the KAO Corp.), Stepantex® VRH 90 (trade name of Stepan Corp.) or Rewoquat® WE 18 (trade name of Witco Surfactants GmbH).

[0014]

The monobasic fatty acids that are conventional and known in this field, which are based on natural vegetable or animal oils with 6-22 carbon atoms, especially 14-18 carbon atoms, can be used as fatty acids for the esterification or transesterification, for instance oleic acid, linoleic acid, linolenic acid and especially rapeseed oil fatty acid, soybean oil fatty acid, sunflower oil

fatty acid, tall oil fatty acid, which can be used by themselves or in mixtures in the form of their glycerides, methyl or ethyl esters or as free acids. In principle, all fatty acids with similar chain distribution are suitable.

[0015]

The content of unsaturated fractions in these fatty acids or fatty acid esters is, if this is necessary, adjusted to the desired iodine number by known catalytic hydrogenation processes or achieved by mixing completely hydrogenated with nonhydrogenated fat components.

[0016]

The iodine number, as a measure of the average degree of saturation of a fatty acid, is the amount of iodine that is used to saturate the double bonds of 100 g of the compound.

[0017]

Fatty acids with iodine numbers in the range from about 40 to 160, but especially rapeseed oil fatty acids, sunflower oil fatty acids, soybean oil fatty acids and tall oil fatty acids with iodine numbers in the range from about 80 to 150 are preferred in accordance with the invention. They are commercial products and are sold by various companies under the relevant trade names.

The esterification or transesterification is carried out by known methods. Here the alkanolamine is reacted with the amount of fatty acid or fatty acid ester corresponding to the desired degree of esterification, optionally in the presence of a catalyst, for example methanesulfonic acid, under nitrogen at 160-240°C and the resulting reaction water or the alcohol is continuously distilled out, where the reaction pressure can optionally be reduced in order to complete the reaction.

[0018]

To produce the esters, the fatty acids and the alkanolamine are reacted in the first stage in a ratio so that a degree of esterification from 1.6 to 2.0 results, in view of the desired industrial application properties of the end products, with it a degree of esterification from 1.8 to 2.0 being especially preferred in accordance with the invention. The resulting compounds are industrial reaction mixtures that are chiefly in the form of diesters.

[0019]

The subsequent quaternization also takes place by known methods. One proceeds in accordance with the invention so that the ester, optionally also using a solvent, preferably

isopropanol, ethanol, 1,2-propylene glycol and/or dipropylene glycol, is mixed at 60-90°C with equimolar amounts of the quaternization agent while stirring, optionally under pressure, and the completeness of the reaction is monitored by monitoring the total amine number.

[0020]

Examples of quaternization agents are organic or inorganic acids, but preferably short-chain dialkyl phosphates and sulfates such as in particular dimethyl sulfate, diethyl sulfate, dimethyl phosphate, diethyl phosphate, short-chain halohydrocarbons, especially methyl chloride.

[0021]

The fatty acids listed below were also used for preparation of the quaternary ammonium compounds in accordance with general formula (I).

Fatty acid I (FA I)

[0022]

Oleic acid with acid number 198-204, iodine number about 95 and C chain distribution

<C 16	about 4%
C 16	about 5%
C 16'	about 5% (monounsaturated)
C 17	about 1%
C 18	about 2%
C 18'	about 70%
C 18''	about 12% (doubly unsaturated)
>C 18	about 2%

Fatty acid II (FA II)

[0023]

Rapeseed oil fatty acid with acid number 196-204, iodine number about 98 and C chain distribution

<C 16	about 2%
C 16	about 5%
C 16'	about 1%
C 17	
C 18	about 3%
C 18'	about 73%

C 18"	about 14%
>C 18	about 2%

### Fatty acid III (FA III)

[0024]

Tall oil fatty acid with acid number 190-198, iodine number about 150 and C chain distribution

C 16	about 1%
C 16'	-
C 17	-
C 18	about 2%
C 18'	about 37%
C 18"	about 60%
>C 18	about 1%

[0025]

The following compounds were used as an example of quaternary ammonium compounds in accordance with formula (I):

Component A1:	TEA: FA I = 1:1.75
Component A2:	TEA: FA II = 1:2.0
Component A3:	MDEA: FA I = 1:1.85
Component A4:	MEIPA: FA II = 1:1.9
Component A5:	MDIA: FA III = 1:1.18

[0026]

Components A1-A5 were quaternized with dimethyl sulfate and they contain 10 wt% isopropanol as solvent. The following references to components A<sup>1</sup> to A<sup>5</sup> mean these quaternized compounds.

Component B1:	R <sup>6</sup> = phenyl, R <sup>4</sup> = H; n = 4
Component B2:	R <sup>6</sup> = i-C <sub>4</sub> H <sub>9</sub> (about 50%)*; n = 0
Component B3:	R <sup>6</sup> = i-C <sub>4</sub> H <sub>9</sub> (about 60%)*; R <sup>4</sup> = H; n = 2.7
Component B4:	R <sup>6</sup> = i-C <sub>4</sub> H <sub>9</sub> (about 60%)*; R <sup>4</sup> = CH <sub>3</sub> ; n = 2.7

\* Sold under the trade name Isanol (Biesterfeld Company, Hamburg).



[0027]

Alkoxylated phenols, which contain one or more alkyl substituents, are used as component B, for example ethoxylated and/or propoxylated phenol, o/m/p-cresol, thymol, p-tert-butylphenol, benzyl alcohol. In addition, optionally alkoxylated branched short-chain alcohols with 3-6 C atoms such as isopropanol, 2-butanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 2-methyl-1-butanol, and their alkoxylation products can additionally be used in accordance with the invention. The degree of alkoxylation is 0 to about 8, where industrial mixtures with an average degree of alkoxylation of 0 or >2.5 up to about 3.5 are preferred in accordance with the invention. The compounds of component B can be used as a mixture with each other in amounts of about 5-30 wt% with respect to the total mixture, preferably in amounts of 10-25 wt%.

[0028]

The preparation of the softeners takes place by emulsifying or dissolving the quaternized compounds A<sup>1</sup>-A<sup>5</sup> while using compounds of general formula B, by adding the relevant individual components to water while stirring. Here the procedures that are in principle conventional in this field can be used.

[0029]

In accordance with the invention one proceeds so that water is present at room temperature, first the dye is added with good agitation, followed by the optionally required antifoam emulsion and finally the softener and component (B) as a mixture or in any order. Then the perfume oil is dispensed and optionally a certain amount of an electrolyte solution in order to reduce the viscosity of the ready-to-use formulation. The softeners in accordance with the invention can contain the said components within the usual limits for this field, for example 15-35 wt% of the compounds of general formula A; 5-30 wt% of at least one of the compounds of general formula B; 0.5-18 wt% of one or more of the conventional auxiliary substances and additives, such as 0.05-1 wt% dyes, 0.05-1 wt% preservatives, 0.1-12 wt% short chain alcohols/diols with 2-6 C atoms, 0.1-1 wt% defoaming agents and especially 0.1-1.5 wt% of an alkali and/or alkaline earth salts; 0.1-1.5 wt% perfume oil, and water to 100 wt% (ad 100).

[0030]

Like the softeners belonging to the prior art, the softeners in accordance with the invention are added to the last rinse cycle at the end of the actual laundry process. The

application concentration, after being diluted with water, is 0.1-10 g softener per liter of rinse water, in each case according to the application.

Examples:

General procedure for producing clear fabric softener formulations:

[0031]

The dye solution is added to demineralized water at room temperature and the quaternary ammonium compound (quat; component A) is slowly mixed into the aqueous phase with continuous stirring. Then component B is added to the mixture of water and quat while stirring, until the mixture has completely dissolved at 20°C. This formulation is then cooled to 4°C and at this temperature must be transparent and clear. Optionally an additional amount of dissolving aid B is added until the mixture is clear at 4°C. At the same time as, before, or after the addition of component B it is possible to add alcohols, preferably glycols with boiling points >120°C, to the mixture in order to increase the flash point.

Then the perfume oil is added while stirring at room temperature and optionally mineral salts in order to adjust the viscosity in the case of high viscosity solutions are added, in order to improve the ability stir the mixture and its ability to flow.

Alkali or alkaline earth metal chlorides in particular can be added as mineral salts in amounts of about 0.1-1.5 wt%, preferably in the form of 10-30 wt% aqueous solutions, in particular an aqueous calcium chloride solution.

Example 1:	
Water	47.4 parts by weight
Dye*	0.8 part by weight
Component A1	30.6 parts by weight
Component B1	18.0 parts by weight
	Product is clear at 20°C
Propylene glycol	2.0 parts by weight
	Product is clear at 4°C
Perfume oil**	0.8 part by weight

Dye\*: 1% aqueous solution Sandolan® Walkblau NBL 150, Sandoz Company

Perfume oil\*: Fragrance® D 650515 W, Haarmann and Reimer GmbH

Example 2:	
Water	47.4 parts by weight
Dye*	0.8 part by weight
Component A4	30.6 parts by weight
Component B1	22.0 parts by weight
	Product is clear at 20°C
Component B2	2.0 parts by weight
	Product is clear at 4°C
Perfume oil**	0.8 part by weight

Dye\*: 1% aqueous solution Sandolan® Walkblau NBL 150, Sandoz Company

Perfume oil\*: Fragrance® D 650515 W, Haarmann and Reimer GmbH

Example 3:	
Water	59.4 parts by weight
Dye*	0.8 part by weight
Component A3	30.6 parts by weight
Component B2	10.0 parts by weight
Perfume oil**	0.8 part by weight
CaCl <sub>2</sub> solution***	1.0 part by weight
	Product is clear at 20°C and at 4°C

Dye\*: 1% aqueous solution Sandolan® Walkblau NBL 150, Sandoz Company

Perfume oil\*: Fragrance® D 650515 W, Haarmann and Reimer GmbH

CaCl<sub>2</sub> solution\*\*\*: 25 wt% in water

Example 4:	
Water	51.4 parts by weight
Dye*	0.8 part by weight
Component A4	30.6 parts by weight
Component B2	6.0 parts by weight
Hexylene glycol	12.0 parts by weight
Perfume oil**	0.8 part by weight
Product is clear at 20°C and at 4°C	

Dye\*: 1% aqueous solution Sandolan® Walkblau NBL 150, Sandoz Company

Perfume oil\*: Fragrance® D 650515 W, Haarmann and Reimer GmbH

Example 5:	
Water	44.9 parts by weight
Dye*	0.8 part by weight
Component A2	30.6 parts by weight
Component B3	12.5 parts by weight
Hexylene glycol	12.0 parts by weight
Perfume oil**	0.8 part by weight
Product is clear at 20°C and at 4°C	

Dye\*: 1% aqueous solution Sandolan® Walkblau NBL 150, Sandoz Company

Perfume oil\*: Fragrance® D 650515 W, Haarmann and Reimer GmbH

Example 6:	
Water	55.4 parts by weight
Dye*	0.8 part by weight
Component A1	30.6 parts by weight
Component B4	10.0 parts by weight
Component B2	6.0 parts by weight
Perfume oil**	0.8 part by weight
Product is clear at 20°C and at 4°C	

Dye\*: 1% aqueous solution Sandolan® Walkblau NBL 150, Sandoz Company

Perfume oil\*: Fragrance® D 650515 W, Haarmann and Reimer GmbH

Example 7:	
Water	46.4 parts by weight
Dye*	0.8 part by weight
Component A5	30.6 parts by weight
Component B4	13.0 parts by weight
Dipropylene glycol	5.0 parts by weight
Perfume oil**	0.8 part by weight
Product is clear at 20°C and at 4°C	

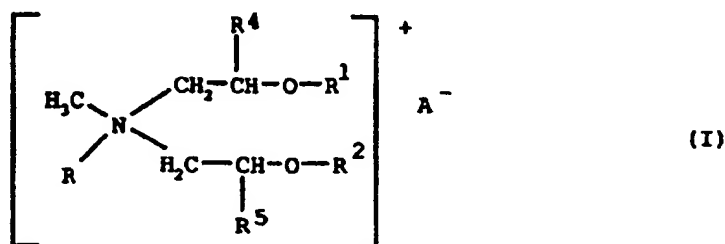
Dye\*: 1% aqueous solution Sandolan® Walkblau NBL 150, Sandoz Company

Perfume oil\*: Fragrance® D 650515 W, Haarmann and Reimer GmbH

### Claims

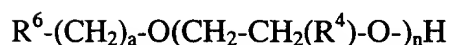
1. Clear fabric softener formulations containing

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European  
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Application Number  
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>6</sup> )
A	US 5 492 636 A (ANSARI H RAHMAN ET AL) February 20, 1996 * Claims 1,2 * * Examples * ---	1-7	C11D1/62 C11D3/20
A	EP 0 082 457 A (HOECHST AG) June 29, 1983 June 29, 1983 * Claims * * Examples * * Page 4, line 21 – line 34 * ---	1-7	
A	US 5 399 272 A (SWARTLEY DONALD M ET AL) March 21, 1995 * Claims 1-12,14-21 * * Examples * ---	1-6	
A	US 5 545 340 A (WAHL ERROL H ET AL) August 13, 1996 * Claims 1-6,13-21 * * Examples 1,8 * * Column 8, line 40 – column 12, line 33 * -----	1-5,7	TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>6</sup> ) C11D
The present search report has been drawn up for all claims.			
Place of search THE HAGUE		Date of completion of the search June 24, 1999	Examiner Neys, P
CATEGORY OF CITED DOCUMENTS			
X:	Particularly relevant if taken alone.	T:	Theory or principle underlying the invention.
Y:	Particularly relevant if combined with another document of the same category.	E:	Earlier patent document, but published on, or after the filing date.
A:	Technological background.	D:	Document cited in the application.
O:	Non-written disclosure.	L:	Document cited for other reasons.
P:	Intermediate document.	&:	Member of the same patent family, corresponding document.

APPENDIX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN  
PATENT APPLICATION NO.

EP 99 10 0154

In this appendix, the patent family members of patent documents listed in the above-referenced European Search Report are indicated.

The data on the family members correspond to the state of the files of the European Patent Office on June 24, 1999  
These data serve only for information and are given without guarantee

Patent document listed in the search report		Date of publication	Member(s) of the patent family		Date of publication
US 5492636	A	February 20, 1996	AU	3608895 A	April 9, 1996
			WO	9609365 A	March 28, 1996
EP 0082457	A	June 29, 1983	DE	3150178 A	June 30, 1983
			AT	20535 T	July 15, 1986
			BR	8207362 A	October 18, 1983
			CA	1188860 A	June 18, 1985
			JP	1655644 C	April 13, 1992
			JP	3020512 B	March 19, 1991
			JP	58109682 A	June 30, 1983
			US	4447343 A	May 8, 1984
			ZA	8209283 A	September 28, 1983
US 5399272	A	March 21, 1995	CA	2138054 A	June 18, 1995
			JP	7229061 A	August 29, 1995
US 5545340	A	August 13, 1996	AU	6271294 A	September 26, 1994
			BR	9405945 A	January 30, 1996
			CA	2157178 A	September 15, 1994
			CN	1121352 A	April 24, 1996
			EP	0687291 A	December 20, 1995
			FI	954084 A	August 31, 1995
			JP	8507766 T	August 20, 1996
			NO	953415 A	November 1, 1995
			WO	9420597 A	September 15, 1994
			US	5562849 A	October 8, 1996
			US	5574179 A	November 12, 1996

For additional details regarding this Appendix: see Official Journal of the European Patent Office No. 12/82

